



ANHARMONIC CONTRIBUTION TO THE SPECIFIC HEAT AT CONSTANT VOLUME OF A ONE DIMENTIONAL SYSTEM OF QUANTUM HARMONIC OSCILLATORS IN THE FIRST DEGREE OF ANHARMONICITY

Dr. Palash Das

Department of Physics, Santipur College, Santipur, West Bengal, India

ABSTRACT

Effect of anharmonicity leads to the exchange of energy between mechanical and thermal vibrations, which can affect the specific heat of a substance. We consider a one dimensional of quantum harmonis oscillators at an absolute temperature T in the presence of a weak anharmonicity and derive an expression for the anharmonic contribution to the specific heat at constant volume.

INTRODUCTION

We consider a system of N (where $N \gg 1$, a basic assumption of Statistical Mechanics) quantum mechanical oscillators in one dimension at an absolute temperature T. The energy levels of an oscillator is approximated as [1]

$$\varepsilon_n = \left(n + \frac{1}{2}\right) h\nu - x \left(n + \frac{1}{2}\right)^2 h\nu \quad (1)$$

where $n=0,1,2,3,\dots$, h is the Planck's constant, ν is the frequency of an oscillator and x is a parameter, which represents the degree of anharmonicity. In this paper, we will find an expression for the anharmonic contribution to the specific heat at constant volume of the system in its first degree of anharmonicity and so $x \ll 1$.

$$\xi = \sum_{n=0}^{\infty} e^{-\beta \varepsilon_n} = \sum_{n=0}^{\infty} e^{-\frac{1}{k_B T} \left[\left(n + \frac{1}{2}\right) h\nu - x \left(n + \frac{1}{2}\right)^2 h\nu \right]} \quad (2)$$

where $\beta = \frac{1}{k_B T}$, k_B is the Boltzmann's constant.

In the first approximation in x , equation (2) can be written as

$$\xi = \sum_{n=0}^{\infty} e^{-\frac{1}{k_B T} \left[\left(n + \frac{1}{2}\right) h\nu \right]} \left[1 + x \frac{h\nu}{k_B T} \left(n + \frac{1}{2}\right)^2 \right] \quad (3)$$

Writing $u = \frac{h\nu}{k_B T}$, we get

$$\xi = \sum_{n=0}^{\infty} e^{-u \left(n + \frac{1}{2}\right)} + xu \left[\sum_{n=0}^{\infty} n^2 e^{-u \left(n + \frac{1}{2}\right)} + \sum_{n=0}^{\infty} n e^{-u \left(n + \frac{1}{2}\right)} + \frac{1}{4} \sum_{n=0}^{\infty} e^{-u \left(n + \frac{1}{2}\right)} \right] \quad (4)$$

Clearly,

$$\sum_{n=0}^{\infty} e^{-u \left(n + \frac{1}{2}\right)} = \frac{e^{-\frac{u}{2}}}{(1 - e^{-u})}, \quad \sum_{n=0}^{\infty} n e^{-u \left(n + \frac{1}{2}\right)} = \frac{e^{-\frac{3u}{2}}}{(1 - e^{-u})^2} \quad \text{and} \quad \sum_{n=0}^{\infty} n^2 e^{-u \left(n + \frac{1}{2}\right)} = e^{-\frac{3u}{2}} \left[\frac{(1 + e^{-u})}{(1 - e^{-u})^3} \right]$$

Substituting the above summations in equation (4), we have

$$\xi = \frac{e^{-\frac{u}{2}}}{(1 - e^{-u})} \left[1 + xu \left\{ \frac{2e^{-u}}{(1 - e^{-u})^2} + \frac{1}{4} \right\} \right] \quad (5)$$

Then the canonical partition function for the system is

$$Z = \xi^N = N \left[-\frac{u}{2} - \ln(1 - e^{-u}) + \ln \left\{ 1 + xu \left(\frac{2e^{-u}}{(1-e^{-u})^2} + \frac{1}{4} \right) \right\} \right] \quad (6)$$

The internal energy of the system is

$$\begin{aligned} \bar{E} &= -\frac{\partial \ln Z}{\partial \beta} = -h\nu \frac{\partial \ln Z}{\partial u} \\ &= -Nh\nu \left[-\frac{1}{2} - \frac{e^{-u}}{(1-e^{-u})} + \frac{x \left\{ \frac{2e^{-u}}{(1-e^{-u})^2} - \frac{2ue^{-u}}{(1-e^{-u})^2} - \frac{4ue^{-u}}{(1-e^{-u})^3} + \frac{1}{4} \right\}}{1 + xu \left\{ \frac{2e^{-u}}{(1-e^{-u})^2} + \frac{1}{4} \right\}} \right] \\ &= E_0 + E_{anharmonic} \end{aligned} \quad (7)$$

where

$$E_0 = Nh\nu \left[\frac{1}{2} + \frac{1}{(e^u - 1)} \right] = \frac{1}{2}Nh\nu + \frac{Nh\nu}{\left(e^{\frac{h\nu}{k_B T}} - 1 \right)} \quad (8)$$

The corresponding specific heat at constant volume is [5]

$$(C_V)_0 = \left(\frac{\partial E_0}{\partial T} \right)_V = Nk_B \frac{\left(\frac{h\nu}{k_B T} \right)^2}{\left[e^{\frac{h\nu}{k_B T}} - 1 \right]^2} \quad (9)$$

as expected.

And

$$E_{anharmonic} = -xNh\nu \left[\frac{\left\{ \frac{2e^{-u}}{(1-e^{-u})^2} - \frac{2ue^{-u}}{(1-e^{-u})^2} - \frac{4ue^{-u}}{(1-e^{-u})^3} + \frac{1}{4} \right\}}{1 + xu \left\{ \frac{2e^{-u}}{(1-e^{-u})^2} + \frac{1}{4} \right\}} \right] \quad (10)$$

The corresponding specific heat at constant volume is

$$\begin{aligned} (C_V)_{anharmonic} &= \left(\frac{\partial E_{anharmonic}}{\partial T} \right)_V = xNk_B u^2 \left(\frac{\partial E_{anharmonic}}{\partial u} \right)_V \\ &= xNk_B u^2 \left[\frac{\partial}{\partial u} \left\{ \frac{D_1(u)}{D_2(u)} \right\} \right] = xNk_B u^2 \left[\frac{1}{D_2} \frac{\partial D_1}{\partial u} - \frac{D_1}{D_2^2} \frac{\partial D_2}{\partial u} \right] \end{aligned} \quad (11)$$

where

$$D_1(u) = \frac{2e^{-u}}{(1-e^{-u})^2} - \frac{2ue^{-u}}{(1-e^{-u})^2} - \frac{4ue^{-u}}{(1-e^{-u})^3} + \frac{1}{4}$$

$$D_2(u) = 1 + xu \left\{ \frac{2e^{-u}}{(1 - e^{-u})^2} + \frac{1}{4} \right\}$$

$$\frac{\partial D_1}{\partial u} = \frac{2e^{-u}}{(1 - e^{-u})^2} \left\{ (u - 2) - \frac{2(1 - u)}{(1 - e^{-u})} + \frac{6u}{(1 - e^{-u})^2} \right\}$$

and

$$\frac{\partial D_2}{\partial u} = x \left[\frac{2e^{-u}}{(1 - e^{-u})^2} \left\{ 1 - u \left(1 + \frac{2e^{-u}}{1 - e^{-u}} \right) \right\} + \frac{1}{4} \right]$$

Substituting these values in equation (11), the anharmonic contribution to the specific heat of the system in the first approximation in the degree of anharmonicity becomes

$$(C_V)_{anharmonic} \cong xNk_B u^2 \left[\frac{2e^{-u}}{(1 - e^{-u})^2} \left\{ (u - 2) - \frac{2(1 - u)}{(1 - e^{-u})} + \frac{6u}{(1 - e^{-u})^2} \right\} \right] \quad (12)$$

This is the result, we want to establish.

For low temperatures, i.e., $u \left(= \frac{h\nu}{k_B T} \right) \gg 1$, equation (12) shows that $(C_V)_{anharmonic} \rightarrow 0$

and for high temperatures, i.e. $u \left(= \frac{h\nu}{k_B T} \right) \ll 1$, $(C_V)_{anharmonic} \approx xNk_B \left(\frac{8}{u} \right) \propto T$.

We end up with the observation that at low temperatures, the anharmonic contribution vanishes and we get the phonon part only. On the other hand, at high temperatures, i.e. at temperatures appreciably above the Debye's temperatures, the anharmonic contribution to the specific heat is linear with temperature as expected. The physical reason of this contribution is because of the anharmonicity of an atom or molecule, which refers to the state, in which the atom or molecule is stretched, oscillated and bent, when the atom or molecule vibrates, so that energy transition occurs from the ground state to the excited state.

REFERENCES

1. J.J.Sakurai, Modern Quantum Mechanics, Addison-Wesley Publishing Company, Inc.
2. Kerson Huang, Statistical Mechanics, Wiley Eastern Limited.
3. Frederick Reif, Fundamentals of Statistical and Thermal Physics, McGraw-Hill Book Company.
4. R.K.Pathria, Statistical Mechanics, Butterworth-Heinemann.
5. Mark W. Zemansky and Richard H. Dittman, Heat and Thermodynamics, McGraw-Hill Book Co.